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A study of the effects of paraffin wax upon the viscosities of lubricating oils

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A STUDY OF THE EFFECTS OF PARAFFIN WAX UPON THE VISCOSITIES OF LUBRICATING OILS

BY

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A

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A STUDY OF THE EFFECTS OF PARAFFIN WAX UPON THE VISCOSITIES OF LUBRICATING OILS

Introduction

The determination of the mean molecular weight of oils and paraffin waxes may have significance as: (1) an important property from a purely research point of view; (2) a step towards structure determination; (3) a study of molecular association with viscosity, making possible the application of well established viscosity binary mixture formulas to oil blends and oil and paraffin wax blends; (4) an aid in the calculations of latent heats for refinery engineering purposes (see A.A. Ashworth's[1] applications of this property); (5) a possible means for identifying bitumens of unknown origin, and determining the approximate proportion of each type in blends; (6) as a means of giving application of Raoult's law for comparison of experimentally determined vapor pressures of oils to the calculated values.

It was with this view of studying viscosity effects of paraffin wax upon lubricating oils and to approximate the probable number of carbon atoms in various melting point paraffin waxes, that this investigation was undertaken.

Various solvents have been used for cryoscopic work on lubricating and crude oils, all of which have been criticised as to their applicability. Hitherto, no solvent for the cryoscopic determination of mean molecular weights of paraffin waxes have been employed, nor has the mean molecular weight of various paraffin wax fractions been published.

It has been stated and it is an apparent fact that paraffin waxes when blended with lubricating oils very greatly reduce the viscosity of the oil at high temperatures. No study of the effect of paraffin wax on viscosity of lubricating oils from a mean molecular weight standpoint has been recorded. The viscosity of an oil and its control is of paramount importance to the lubration engineer, and any information leading to a more complete knowledge of an oil will be of some value.

Binary mixtures formulas for lubricating oils have been proposed and given application. However the calculated values show in nearly all cases a deviation from the experimantal values. Formulas giving the closest agreeing values embodies the molecular weights of the components. As these molecular weights were usually determined at relatively low temperatures as compared to the temperature at which the viscosity of the mixtures

was determined, it seems possible that a higher temperature determination of the mean molecular weight might give closer agreement between the calculated blend viscosity and the experimental value.

It was with these views in mind that this research was undertaken.

HISTORICAL CONSIDERATIONS

Mean Molecular Weights:

Hitherto comparatively little work has been done on the mean molecular weight of lubricating oils and less work has been done on their mole fraction blends. In 1923 Wilson and Wylde[1] published a paper on the "Vapor Tension of Solvents". In order to apply Raoult's law to check experimental vapor pressures, they determined the mean molecular weight of hydrocarbon lubricating oils. Benzene was used as a solvent and the Beckmann cryoscopic method employed. C.F. Mabery[1] stated that for high molecular weights benzene was unsatisfactory and recommended stearic acid. As no attempt was made to dry the benzene solvent, this may have been a source of error.

Roberts and Bury[21] have shown that the freezing point of nitrobenzene altered on standing, but recommended it for cryoscopic work when cautions for drying were taken. This change of freezing point was undoubtedly due to moisture absorption.

Nitrobenzene dried with anhydrous sodium sulfate was used by A.H. Steed[22] for cryoscopic determination of the mean molecular weights of light petroleum fractions.

In 1931 Gullic[2] published a paper on "The Determination of Mean Molecular Weights of Lubricating Oils by Improved Cryoscopic Methods". He followed a procedure very similar to the one of Steed with certain modifications necessary when dealing with more viscous oils. Benzene and nitro-benzene were used as solvents. An electrical platinum resistance thermometer and a Beckmann thermometer were employed and it gave very close checks for the mean molecular weights. Two types of oils were used: asphaltic Venezulean and paraffin Pennsylvanian crudes. Plots were made of freezing point lowering against mean molecular weight. Extrapolation to zero depression gave a value what was called the mean molecular weight at zero concentration. Plots made in this way were not horizontal lines, but sloped. This was discussed and attributed to mixed crystal formation rather than to association.

Benzene was found to be a satisfactory solvent for cryoscopic determination of mean molecular weights of oils by Robinson and Oakey.[4]

Epperson and Dunlap[17] in 1932 published a paper on the "Relationship between the Mole Fraction and the Absolute Viscosity of Blended Lubricating Oils". In this the mean molecular weights

of light and heavy lubricating oils were determined and absolute viscosity mole fraction graphs were made. Three solvents were used: benzene, nitro-benzene, and ethylene dibromide. A dry air train was at all times connected to their apparatus to insure a constant amount of moisture as an impurity. This method for keeping the solvent dry has been criticised by Roberts and Bury[21], but very close checks were obtained using the three solvents. Ethylene dibromide was found to be a very satisfactory solvent for cryoscopic work on oils, it being only slightly hydroscopic in comparison to benzene and nitro-benzene. A further study of the mole fraction relationship of blended lubricating oils was made by Moore[18]. He used ethylene dibromide as a solvent and a dry air train.

Methods other than the cryoscopic method have been used to determine mean molecular weights of non-homogeneous mixtures with less satisfaction. Vapor density method[33] as in the classical Victor Meyer experiment, has been used with some success on relatively high volatile hydrocarbons, but it is obviously not suitable for the determination of the mean molecular weights of oils due to their low volatility. Ormondy and Craven[3] in their

determination of the mean molecualr weight of petroleum fractions used the Victor Meyer method obtaining erratic results when it was necessary to heat the bulb to high temperatures. High temperature determinations gave indications of cracking.

Viscosity:

Viscosity is the resistance of a material or mixture to flow when a force is exerted upon it. For practical purposes of calculation the viscosity is that force which will move a unit area of plane surface with unit speed relative to another parallel plane surface from which it is separated by a layer of unit thickness. Absolute viscosity is that force in dynes required to move a surface one cm. distant with a velocity of 1 cm. per sec. Absolute viscosity is expressed in poises, one dyne-second per square cm. is one poise. A poise is that force, which, when exerted tangentially on 1 sq. cm. surface of wither of two horizontal planes 1 cm. apart, will move one plane at the rate of 1 cm. per sec. in reference to the other plane, the in between space being filled with the liquid.

Newmann[8] made the deduction from Poiseiulle's[24] formula, assuming that there is no slip at the surface

of the capillary, that the liquid flows steadily, that there are no eddies or turbulent motion, and that there is no kinetic energy efflux:

$$n = \frac{h\ g\ D\ t\ d}{8lV}$$

where:

n is absolute viscosity in poises
h is head in centimeters
g is acceleration of gravity (981 cm/sec.^{2})
D is diameter of tube in centimeters
d is density of liquid in grams per cc.
l is length of capillary in centimeters
V is volume of liquid in cc.

Many modifications of this formula have been made depending upon the conditions under which it is applied.

Although, the value of "n" may be calculated quite definitely from a given formula when certain conditions are known, formulas for the determination of "n" for binary mixtures when the viscosity and composition of the components are known, do not apply with the same degree of accuracy. Much experimentation has been done in an attempt to discover some mathematical relationship between the viscosity of a mixture and the viscosity of the components. There seems to be no mathematical equation which fits the available data. Blending of oils 25, 26, 27, 20, 28 is done largely by

the use of charts prepared for specific types of oils to be blended. Commercial application could be made of a formula expressing the accurate viscosity of a blend.

No linear formula can be utilized since in every curve there is a divergance greater or less than that required by the mixture law. Einstein[8,29] reasoned that there should be a linear increase in viscosity. This was found to be true only for low concentrations.

Dunstan's[8] investigation led him to believe that there are three types of binary mixture viscosity concentration curves: I. Those that obey approximately the law, being concave to the axis of percentage composition. II. Those which exhibit definite maxima. III. Those which exhibit a minimum point.

Findaly[8] proposed the formula:

$$\frac{1}{n} = \frac{1}{n_1} + \frac{1}{n_2}$$

where n_1 and n_2 refer to the viscosities of the respective components and v_1 and v_2 the respective volumes contained 1 cc of the mixture. Divergence of the formula from the ordinary law of mixtures was considered to be of importance as an indicator of the magnitude of the interaction of the components.

Bingham[8,30] showed that mixtures following type (1) gave nearly linear fluidity and concluded that fluidities were additive. Krücker and Phasel[8] suggested the same equation with weight composition units. Arrhenius[6] proposed the logarithmic formula:

$$\log \eta = v_1 \log \eta_1 + v_2 \log \eta_2$$

This formula was found to hold when one component was present to the extent of 60% or more. In view of the facts Kendall modified Arrhenius' formula:

$$\log \eta = x_1 \log \eta_1 + x_2 \log \eta_2$$

where x_1 and x_2 are the molecular percentage of the components in the mixture. Kendall[8] also tried a molecualr fluidity formula, but he did not find it superior to the modified Arrhenius formula.

Kendall and Monroe, after experimenting with eighty-four binary mixtures, proposed the cube root equation:

$$(\eta)^{1/3} = x_1(\eta)^{1/3} + x_2(\eta)^{1/3}$$

where x_1 and x_2 are the mols fractions and η_1 and η_2 are viscosities of the components.

Ogden Fitz Simons[31] has found the equation:

$$\log \log (K + .8) = x \log \log (K_1 + .8) + (1-x) \log \log (K_2 + .8),$$

where K, K_1, and K_2 is the kinematic viscosity of

the blend and two components respectively, X is the volumw fraction, to possess a high degree of accuracy. Aside from accuracy this equation is advantageous as neither gravities nor molecular weights are required as in the Kendall and Monroe equation, and when it is used with the Log Log function (See Table X) it is easily applied.

EXPERIMENTAL PART

Materials Used

The ethylene bromide was furnished by the Texaco Salt Products Co. of Tulsa, Okla. It was redistilled and the middle portion having a distilling range of .25° C was stored in a dark glass bottle containing fused $CaCl_2$.

Four closely cut fractions of paraffin wax having melting points of 109.5°F, 125.5°F, 133.5°F, and 141°F respectively were furnished by Messers Sullivan, McGill and French of the Standard Oil Company (Indiana) at Whiting, Ind. The wax from which these samples were taken was 125°F. melting point refinery wax. It was sweated from intermediates and did not contain the highest melting waxes separated by pressing.

The commercial "Parowax" was obtained from the Standard Oil Company of Indiana. It was slowly melted, heated to 130°C for an hour and a half under a pressure of 5 cm. of mercury while dry CO_2 was allowed to bubble through the molten liquid. It was cooled in an evaporating dish and stored in a wide mouth bottle.

The two mid-continent lubricating oils were furnished by the Shell Petroleum Corporation of Wood River, Ill. One was a neutral oil and the other a bright stock.

A neutral and a bright stock samplewere furnished by the Kendall Oil Co. of Bradford, Penn.

The camphor was a commercial Grade. It was resublimed before using.

The nitro-benzene was of C.P. grade obtained from the Central Scientific Co. It was stored over fused $CaCl_2$ for a week, purified by crystallinzing half of a given volume, distilling the crystallized portion and using the middle portion having a distilling range of .25°C. Half of the distilled portion was separated by recrystallization and stored in a glass stoppered bottle half full of fused $CaCl_2$.

The stearic acid was a commercial grade obtained from the Mallinckrodt Chem. Works. It was recrystallized twice from commercial benzene which had been treated with conc. sulphuric acid, then washed with water, dilute sodium carbonate, water, dryed over fused $CaCl_2$, and distilled, that portion distilling between 80°- 90° C being used. The recrystallized stearic acid was dryed by slowly heating to 140° - 150°C under 8 cm. of mercury until most of the benzene passed over. The pressure was then reduced to 1 cm. of mercury and a stream of dry CO_2 bubbled through the molten liquid for one hour. The dry acid was then poured into an evaporating dish, cooled, ground to a coarse sand size, and s stored in a wide mouth cork stoppered bottle.

Apparatus

For the cryoscopic determination of freezing point lowering the regular Beckmann[9,10,14,15] freezing point apparatus, equipped with a mechanical stirrer and a dry air train, was employed. The air was dried by passing through two sulphuric acid bubbling towers, a $CaCl_2$ drying tower, and a cotton dust filter. For low temperature work, the temperature of the cooling bath was regulated by the addition of ice, and for high temperature work an immersion electric heater was used. An auxiliary bath was used in both cases. For low temperatures the auxiliary bath was used to cool the freezing point tube to some definite temperature before placing it in the regular cooling bath, and for high temperatures it was used to melt the solidified solvent and heated it to some definite temperature. The freezing point tube consisted of a glass tube 8" by 1" equipped with a side neck. Five and a half inches of the tube was completely enclosed by an air mantle and at least a distance of $\frac{1}{4}$" from the sides of the mantle. The stirrer consisted of two corrugated platinum ring paddles attached to two wire guides fastened at the top to a heavy iron-nickle alloy ring. The heavy ring rested on a copper lead which was mechanically driven and pulled the paddles up and then

allowing them to go down by their own weight.

Viscosities were determined by means of a Standard Universal Viscosimeter manufactured by the Tagliabue Manufacturing Co. The water bath of the Viscosimeter was heated by an electric immersion heater. An ordinary stop watch graduated in .2 seconds was used for timing.

Standard A.P.I. hydrometers manufactured by the Tagliabue Manufacturing Co. were used to determine the specific gravities of the oils, wax, and blends.

EXPERIMENTAL PROCEDURE

Cryoscopic Determination of Mean Molecular Weight:

The cooling mixture of water and ice was maintained between 1°- 2° C below the freezing point of the ethylene dibromide. The Beckmann thermometer was adjusted so that at the freezing point of the solvent the mercury thread was at about the middle of the scale. The freezing point tube was accurately weighed and then about 20 cc of ethylene bromide was quickly added, the tube closed with a stopper, and rapidly reweighed. The thermometer and stirrer were then placed into the tube and the whole immersed directly into the cooling bath. Dry compressed air was passed through the stirrer entrance and a very slight pressure maintained throughout the determination. The velocity at which the air passes through was determined by the rate of bubbling in the sulphuric towers and was regulated by means of a hand operated release valve and by a cut out release.

The freezing point of the solvent was then determined by direct cooling in the bath. When the solvent began to freeze out, the tube was quickly dryed and placed in the air mantle and stirred slowly, about 45 to 50 strokes per minute, until the temperature became constant. This reading

was noted. The tube was then withdrawn from the mantle, warmed slightly with the hand until all of the solid disappeared, care being taken that the mercury did not go off of the scale, placed in the air mantle of an auxiliary bath which was maintained at a few degrees below the working bath and the temperature slowly brought to within .5° C of the previously determined freezing point while stirring with the hand. The tube was quickly transferred to the air mantle of the working bath and slowly stirred by the mechanical stirrer. When the temperature had fallen to about .2° C below the previously determined freezing point, it was stirred more rapidly, about 55 to 60 strokes per minute, until the temperature began to rise, at which time it was again stirred more slowly. The rate of stirring was varied or kept constant by means of a rheostat in series with the motor. As the temperature raised, thermometer readings were taken every few seconds, the thermometer being lightly tapped before each reading. The final high reading was recorded as the freezing point. By means of a small lens readings were taken to .002° C. Three or more concordant readings were taken and no reading that

varied more than .004° from the mean was used.

A weighed amount of substance was added through the side arm of the freezing tube. A sufficient quantity was added to produce a lowering of from 1.5° to 0.3°. After the added substance dissolved the freezing point of the solvent was redetermined as previously described. The final difference between this reading and the one for the pure solvent is the freezing point lowering.

The molecular weight of the solute was the calculated from the Formula: $M = \frac{Kw}{dW}$, where w is the weight of the solute, W is the weight of the solvent, K is a constant dependent upon the solvent, and d is the lowering of freezing point in ° C.

The values of K for ethylene bromide were determined over a freezing point lowering range of 0.1°to 0.6° using camphor. A graph was plotted with lowering along the abscessa and K along the ordinate. Values of K for various lowerings were taken from this graph.

Freezing point determinations using stearic acid as a dolvent were carried out in a similar manner. The cooling liquid was water maintained

at 50.5° to 51.0° C by means of an electric immursion heater controlled by a hand switch. Two baths were used, one served as a freezing bath and the other as a melting bath. The thermometer was set so that the freezing point would be read on the lower third of the scale.

The freezing point tube was accurately weighed and approximately 18 gms. of stearic was roughly weighed on a balance accurate to the 0.1 gm., placed in the tube and the whole accurately reweighed. The freezing point of the stearic acid was determined by direct cooling in the bath. When it began to crystalize out, the tube was quickly dryed and placed in the air jacket and slowly stirred until the temperature became constant. The tube was then withdrawn from the mantle, placed directly into the melting bath and heated with hand stirring until the mercury raised within two degrees of the top of the scale. The tube was then quickly dryed, placed in the air mantle of the melting bath and left there until the temperature raised within 0.5° of the top of the scale. The tube was then withdrawn and quickly placed in the air mantle of the cooling bath, stirred slowly

with the mechanical stirrer until the mercury dropped 0.2° below the previously determined freezing point. The liquid was then vigorously stirred until the temperature began to raise, at which time it was stirred more slowly. Readings were taken every few seconds, tapping lightly with the finger before each reading. The highest reading was recorded. Three or more concordant readings were taken. Only those that vary more than .005° from the mean were used.

The molecular weight was calculated from the formula given above. K, for the stearic acid was determined using nitrobenzene.. A capillary pipette with a drying tube filled with fused $CaCl_2$ attached to the mouth end was used to deliver the nitrobenzene to the stearic acid through the side neck.

COMPOUNDING OF BLENDS

Six series of blends were prepared, four in which the "Parowax" was blended with oils and two in which oils were blended. Blends of oils and wax of 10, 15, 20, 30, 50 and 75 mole percent, and oils of 15, 30, 50, 70 and 85 mole percent of each component were made. two hundred gram blends were made by weighing the calculated mole percent of the components on a large balance accurate to 0.1 gram. The blend was slowly heated with agitation by a high speed electric stirrer to 250° F and maintained at this temperature for ten minutes. Once the wax blends were mixed, their viscosity was determined before allowing to solidify.

Viscosity Determinations:

The viscosities of all oils, wax, and blends were determined by the regular A.S.T.M. method by means of the Sayboldt Standard Universal Viscosimeter. The Sayboldt viscosities were converted to absolute viscosities by means of Herschel's[23] equations:

n/D is $.00226t - \frac{1.96}{t}$ where t is less than 100 sec.

n/D is $.00220 - \frac{1.35}{t}$ where t is more than 100 sec.

Specific Gravity Determinations:

Specific gravity was determined by means of A.P.I. Beaume' hydrometers graduated accurately to 0.1 Beaume'. Gravities were taken at convenient temperatures, converted to 60°F and then to the temperature at which the viscosity was determined. Gravity conversions were made on the assumption that the change per degree F was .00042 gms./cc.

DATA

The results of mean molecular weight determinations on the original oil and wax samples are shown in Tables two and three. Each of the molecular weights and viscosities were checked by three or more independent determination.

Tables three to ten show the composition, viscosity, density, and calculated viscosity values for each oil blend. Table ten is a reprint of a complied table used by Fritz Simons for the calculating of viscosities of oil blends. Table eleven is taken from Mosse's thesis and shows the effect of calculating $(n)^{1/3}$ using mean molecular weights as determined by using ethylene dibromide and stearic acid as solvents.

Plate I shows the variation of K in the formula: $\eta = Kw/dW$ with freezing point lowering. Plate II to VII shows the variation in viscosity with mole composition. Mole percent is plotted as abscissa and cube root of the absolute viscosity as ordinate.

Table No. I

Nomenclature	Designation
Shell 200 Golden Neutral	A
Shell "H" Bright Stock	D
Kendall Neutral	I
Kendall Bright Stock	J
Parowax	W

TABLE II

Results of Determinations on Original Wax Samples

Melting point	Mean Mol. Wt.	Probable C atoms
Wax (109.5° F)	326	23
Wax (125.5° F)	365	26
Wax (133.5° F)	370	26
Wax (141.0° F)	397	28
Parowax	385	27

TABLE III

Results of Tests and Determinations on Original Oils and Wax

Substance	Mean Mol. Wt. Stearic Acid	Mean Mol. Wt. $C_2H_4Br_2$	Density Grams/cc 210° F	Saybolt Sec. 210° F
A	334	381 (395*)	.8576	44.7
D	539	705 (659*)	.8546	159.3
I	390	455*	.8135	46.0
J	738	996*	.8388	158.0
W	385	---	.7489	38.0

Note: Values marked * are those taken from Moore's Molecular Weight and Absolute viscosity of Lubricating oils.

TABLE III (Cont.)

Results of Tests and Determinations on Original Oils and Wax

Substance	Kinematic Viscosity 210°F	Absolute Viscosity 210°F	Cube Root Abs. Visc. 210°F
A	.0574	.0492	.3665
D	.3457	.2792	.6536
I	.0616	.0501	.3687
J	.3390	.2843	.6576
W	.0346	.0259	.2956

Substance	Density Grams per cc 170°F	Kinematic Viscosity 170°F	Absolute Viscosity 170°F	Cube Root Absolute Viscosity 170°F	Say. Sec. 170° F
A	.8744	59.3	.0884	.4455	59.3
B	.8714	.7794	.6792	.8790	356
I	.8303	.1031	.0856	.4407	60
J	.8556	.7463	.6385	.8611	341
W	.7657	.0501	.0384	.3372	42.5

TABLE IV

Blends of Shell 200 Golden Neutral and Parowax

Blend No.	Mole Comp.	Weight Comp.	Vol. percent 210°F	Density Grams per cc 210°F	Saybolt Seconds 210°F	Fits Simons Calc Sec. 210°F
1.	.10W .90A	22.72W 177.28A	12.79W 87.21A	.8435	43	43.5
2.	.15W .85A	33.76W 166.24A	18.86W 81.14A	.8394	42	42.9
3.	.20W .80A	44.74W 155.26A	24.81W 75.19A	.8325	41.6	42.5
4.	.30W .70A	66.18W 153.82A	36.15W 63.85A	.8211	40.6	41.7
5.	.50W .50A	107.11W 92.89A	56.90W 44.10A	.8008	39.4	40.3
6.	.75W .25A	154.99W 45.01A	79.77W 20.23A	.7630	38.4	38.9

Blend No.	Kinematic Viscosity 210°F	Abs. Vis. 210°F	$(n)^{1/3}$ 210°F	Calc. $(n)^{1/3}$ Kendall Equation 210°F	Density Grams per cc 210°F
1.	.0518	.0437	.3524	.3594	.9065
2.	.0485	.0407	.3440	.3558	.9024
3.	.0471	.0392	.3398	.3543	.8955
4.	.0437	.0359	.3298	.3452	.8841
5.	.0395	.0317	.3164	.3310	.8638
6.	.0360	.0275	.3017	.3133	.8360

Table IV (Continued)

Blends of Shell 200 Golden Neutral and Parowax

Blend No.	Vol. % 170°F	Density Grams per cc 170°F	Saybolt Seconds 170°F	Fitz Simons Calc. Sec. 170°F	Kinematic Viscosity 170°F	Abs. Viscosity 170°F
1.	12.76W 87.24A	.8603	54.1	55.9	.0862	.07415
2.	18.82W 81.18A	.8562	52.2	54.5	.0806	.0690
3.	24.75W 75.25A	.8493	51	53.2	.0770	.0654
4.	36.09W 63.91A	.8379	48.2	51	.0685	.0574
5.	56.83W 43.17A	.8176	45.5	47.6	.0600	.0491
6.	79.72W 20.28A	.7898	43.7	44.6	.0541	.0427

Blend No.	1/3 (n) 170°F	Calc. 1/3 (n) Kendall Equation 170°F
1.	.4201	.4347
2.	.4102	.4292
3.	.4025	.4238
4.	.3857	.4130
5.	.3661	.3913
6.	.3497	.3643

TABLE V

Blends of Shell "H" Bright Stock and Parowax

Blend No.	Mole Comp.	Weight Comp.	Vol. % 210°F	Density Grams per cc 210°F	Saybolt Seconds 210°F	Fitz Simons Calc. Sec. 210°F
7.	.10W .90D	14.70W 185.30D	8.27W 92.73D	.8467	121.6	124.5
8.	.15W .85D	22.35W 177.65D	12.52W 87.48D	.8417	108	110.2
9.	.20W .80D	33.12W 166.88D	18.15W 81.85D	.8394	96	96.9
10.	.30W .70D	46.87W 153.13D	61.21W 38.79D	.8142	78	81.8
11.	.50W .50D	83.33W 116.67D	44.83W 55.17D	.8123	56.2	58.3
12.	.75W .25D	136.36W 63.64D	70.91W 29.09D	.7792	44	44.8

Blend No.	Kinematic Viscosity 210°F	Abs. Vis. 210°F	$(n)^{1/3}$ 210°F	Calc. $(n)^{1/3}$ Kendall Equation 210°F	Density Grams per cc 210°F
7.	.2564	.2171	.6010	.6278	.9097
8.	.2251	.1894	.5743	.6073	.9047
9.	.1966	.1642	.5475	.5900	.9024
10.	.1513	.1231	.4975	.5532	.8772
11.	.0923	.0750	.4217	.5796	.8753
12.	.0551	.0429	.3503	.3876	.8422

Table V (Continued)

Blends of Shell "H" Bright Stock and Parowax

Blend No.	Vol. % 170°F	Density Grams per cc 170°F	Sayblot Seconds 170°F	Fitz Simons Calc. Sec. 170°F	Kinematic Viscosity 170°F	Abs. Viscosity 170°F
7.	8.29W 91.71D	.8635	249.9	260	.5443	.4700
8.	12.55W 87.45D	.8585	211	220	.4578	.3930
9.	18.19W 81.81D	.8562	184	184.9	.3975	.3403
10.	25.88W 74.12D	.8310	134	144	.2847	.2366
11.	44.90W 55.10D	.8291	81.5	87.8	.1603	.1329
12.	70.97W 29.03D	.7960	52.7	55.7	.0821	.0653

Blend No.	$1/3$ $(\#)_{170°F}$	Calc. $1/3$ (n) Kemdall Equation 170°F
7.	.7775	.8248
8.	.7325	.7977
9.	.6982	.7706
10.	.6185	.7165
11.	.5093	.6081
12.	.4028	.4726

TABLE VI

Blends of Kendall Neutral and Parowax

Blend No.	Mole Comp.	Weight Comp.	Vol. % 210°F	Density Grams per cc 210°F	Saybolt Seconds 210°F	Fitz Simons Calc. Sec. 210°F
13.	.10W	119.77W	10.60W	.8069	45	44.8
	.90I	180.23I	89.40I			
14.	.15W	29.63W	15.89W	.8056	43.2	44.2
	.85I	170.37I	84.11I			
15.	.20W	39.58W	21.13W	.8017	42.7	43.4
	.80I	160.42I	78.87I			
16.	.30W	59.46W	31.48W	.7991	41.5	42.7
	.70I	140.54I	68.52I			
17.	.50W	98.84W	51.48W	.7757	40.0	40.9
	.50I	101.16I	48.52I			
18.	.75W	149.51W	76.28W	.7614	38.4	39.3
	.25I	50.49I	23.72I			

Blend No.	Kinematic Viscosity 210°F	Abs. Vis. 210°F	$(n)_0^{1/3}$ 210°F	Calc. $(n)^{1/3}$ Kendall Equation 210°F	Density Grams per cc 60°F
13.	.0583	.0470	.3611	.3614	.8699
14.	.0525	.0423	.3484	.3577	.8686
15.	.0508	.0407	.3441	.3540	.8647
16.	.0468	.0374	.3344	.3468	.8621
17.	.0416	.0323	.3185	.3321	.8387
18.	.0360	.0274	.3010	.3143	.8244

Table VI (Continued)

Blends of Kendall Neutral and Parowax

Blend No.	Vol. % 170°F	Density Grams per cc 170°F	Saybolt Fits Seconds 170°F	Simons Calc. Sec. 170°F	Kinematic Viscosity 170°F	Abs. Viscosity 170°F
13.	10.62W 89.38I	.8237	56	57.9	.0917	.0755
14.	15.86W 84.14I	.8224	53.7	55.7	.0850	.0699
15.	21.10W 78.90I	.8185	52.8	54.4	.0824	.0674
16.	31.44W 68.56I	.8159	50.5	52.2	.0755	.0616
17.	51.44W 48.56I	.7925	47.2	48.6	.0653	.0518
18.	76.25W 23.75I	.7782	43.9	45	.0548	.0426

Blend No.	$(n)^{1/3}$ 170°F	Calc $(n)^{1/3}$ Kendall Equation 170°F
13.	.4227	.4303
14.	.4120	.4252
15.	.4070	.4199
16.	.3950	.4100
17.	.3728	.3889
18.	.3484	.3630

TABLE VII

Blends of Kendall Bright and Sarowax

Blend No.	Mole Comp.	Weight Comp.	Vol. % 210°F	Density Grams per cc 210°F	Saybolt Seconds 210°F	Fitz Simons Calc. Sec. 210°F
19.	.10W .90J	10.95W 189 .05J	6.09W 93.91J	.8400	128.7	122.7
20.	.15W .85J	22.47W 77.53J	9.32W 90.68J	.8309	117.5	122.7
21.	.20W .80J	23.08W 176.92J	12.74W 87.26J	.8253	108	110
22.	.30W .70J	36.54W 163.46J	20.20W 79.70J	.8220	90	91.4
23.	.50W .50J	68.56W 131.43J	36.87W 63.13J	.8110	64.7	66.9
24.	.75W .25J	122.03W 77.97J	63.67W 36.33J	.7831	47.3	47.5

Blend No.	Kinematic 210 210°F	Abs. Vis. 210°F	$(n)^{1/3}_{210^\circ F}$	Calc. $(n)^{1/3}$ Kendall Equation 210°F	Density Grams per cc 210°F
19.	.2726	.2290	.6118	.6214	.9030
20.	.2470	.2052	.5896	.6033	.8939
21.	.2251	.1857	.5704	.5852	.8883
22.	.1817	.1493	.5306	.5490	.8850
23.	.1161	.0941	.4549	.4766	.8741
24.	.0656	.0514	.3578	.3861	.8461

Table VII (Continued)

Blends of Kendall Bright and Parowax

Blend No.	Vol. % 170°F	Density Grams per cc 170°F	Saybolt Seconds 170°F	Fitz Simons Cals. Sec. 170°F	Kinematic Viscosity 170°F	Abs. Viscosity 170°F
19.	6.07W 93.93J	.8568	258	268.7	.5624	.4818
20.	9.30W 90.60J	.8477	235	241	.5113	.4334
21.	12.72W 87.28J	.8421	229	214	.4979	.4193
22.	19.98W 80.02J	.8388	161	168	.3458	.2895
23.	36.82W 63.18J	.8279	100	104	.2065	.1709
24.	63.62W 36.37J	.7999	60	61.3	.1031	.0825

Blend No.	$(n)^{1/3}$ 170°F	Calc. $(n)^{1/3}$ Kendall Equation 170°F
19.	.7840	.8087
20.	.7568	.7825
21..	.7485	.7562
22.	.6621	.7039
23.	.5550	.5991
24.	.4353	.4682

TABLE VIII

Blends of Shell 200 Golden Neutral and Kendall Bright

Blend No.	Mole Comp.	Weight Comp.	Vol. % 210°F	Density Grams per cc 210°F	Saybolt Seconds 210°F	Fitz Simons Calc. Sec. 210°F
25.	.15A .85J	14.79A 185.21J	7.24A 92.76J	.8371	137.5	135.7
26.	.30A .70J	32.56A 167.44J	15.98A 84.01J	.8406	119	113.3
27.	.50A .50J	62.42 137.58	30.74A 69.26J	.8452	95	88
28.	.70A .30J	102.85A 97.15J	50.87A 49.12J	.8479	71	66.1
29.	.85A .15J	144.00A 56.00J	71.55A 28.45J	.8511	56.5	54.3

Blend No.	Kinematic Viscosity 210°F	Abs. Vis. 210°F	$(n)^{1/3}_{210°F}$	Calc. $(n)^{1/3}$ Kendall Equation 210°F	Density Grams per cc 60°F
25.	.2926	.2450	.6257	.6139	.9001
26.	.2505	.2105	.5949	.5702	.9036
27.	.1942	.1641	.5475	.5120	.9082
28.	.1330	.1127	.4831	.4538	.9108
29.	.0932	.0793	.4296	.4101	.9141

Table VIII (Continued)

Blends of Shell 200 Golden Neutral and Kendall Bright

Blend No.	Vol. % 170°F	Density Grams per cc 170°F	Saybolt Seconds 170°F	Fitz Simons Calc. Sec. 170°F	Kinematic Vis. 170°F	Abs. Vis. 170°F
25.	7.24A 92.76J	.8539	283	285	.6178	.5275
26.	15.98A 84.02J	.8574	243	230	.5291	.4536
27.	30.74A 69.26J	.8620	179	167	.3863	.3330
28.	50.88A 49.12J	.8646	123	113	.2596	.2244
29.	71.55A 27.45J	.8679	87	82	.1742	.1512

Blend No.	$\sqrt[1/3]{(n)}$ 170°F	Calc. $\sqrt[1/3]{(n)}$ Kendall Equation 170°F
25.	.8080	.7987
26.	.7684	.7364
27.	.6931	.6533
28.	.6077	.5701
29.	.5527	.5077

TABLE IX

Blends of Shell "H" Bright Stock
And Kendall Neutral

Blend No.	Mole Comp.	Weight Comp.	Vol. % 210°F	Density Grams per cc 210°F	Saybolt Seconds 210°F	Fitz Simons Calc. Sec. 210°F
30.	.15I .85D	22.64I 177.35D	11.82I 88.18D	.8483	127	84.2
31.	.30I .70D	47.34I 152.65D	24.57I 75.53D	.8446	102.2	74.4
32.	.50I .50D	83.96I 116.04D	43.18I 56.82D	.8300	78.3	63.2
33.	.70I .30D	125.60I 74.40D	63.94I 36.06D	.8297	61.2	55.2
34.	.85I .15D	160.78I 39.22D	81.15I 18.85D	.8236	52	50.1

Blend No.	Kinematic Viscosity 210°F	Abs. Vis. 210°F	$(n)^{1/3}$ 210°F	Calc. $(n)^{1/3}$ Kendall Equation 210°F	Density Grams per cc 60°F
30.	.2687	.2280	.6109	.6193	.9113
31.	.2116	.1787	.5633	.5751	.9076
32.	.1520	.1265	.5016	.5161	.9030
33.	.1064	.0883	.4453	.4572	.8927
34.	.0800	.0659	.4039	.4129	.8866

Table IX (Continued)

Blends of Shell "H" Bright Stock and Kendall Neutral

Blend No.	Vol. % 170°F	Density Grams per cc 170°F	Saybolt Seconds 170°F	Fitz Simons Calc. Sec. 170°F	Kinematic Viscosity 170°F	Abs. Vis. 170° F
30.	11.81I 88.19D	.8651	267	265	.5824	.5038
31.	24.55I 75.45D	.8614	208	197	.4511	.3886
32.	43.16I 56.83D	.8568	141	134	.3004	.2575
33.	63.92I 36.08D	.8465	97.5	93	.2065	.1748
34.	81.14I 18.86D	.8404	75.1	73.6	.1517	.1275

Blend No.	$(n)^{1/3}_{170^\circ F}$	Calc. $(n)^{1/3}$ Kendall Equation 170°F
30.	.7957	.8132
31.	.7297	.7475
32.	.6362	.6598
33.	.5591	.5722
34.	.5033	.5064

TABLE Σ_{31}

Log Log (X + .5) x 10,000

Compiled from A.S.T.M. equations[32]
and 7 place logarithm tables

Saybolt Vise.	0	1	2	3	4	5	6	7	8	9
30	-	-	-	-	-	-3038	-2625	-2326	-2013	-1778
40	-1574	-1396	-1238	-1096	-0968	-0851	-0745	-0648	-0555	-0471
50	-0391	-0317	-0245	-0182	-0120	-0061	-0006	+0048	0099	0148
60	0194	0239	0281	0325	0362	0400	0437	0473	0507	0540
70	0573	0604	0634	0664	0692	0720	0747	0774	0800	0825
80	0849	0873	0896	0919	0942	0963	0985	1006	1026	1046
90	1066	1085	1104	1122	1141	1158	1176	1193	1210	1227
100	1243	1258	1274	1289	1303	1317	1332	1346	1359	1363
110	1386	1400	1413	1426	1438	1451	1463	1476	1488	1500
120	1511	1523	1534	1546	1557	1568	1579	1591	1601	1612
130	1622	1632	1642	1653	1663	1673	1682	1692	1702	1712
140	1722	1731	1739	1748	1758	1767	1776	1785	1793	1802
150	1810	1819	1827	1836	1844	1852	1860	1868	1876	1884
160	1892	1900	1908	1916	1923	1930	1938	1946	1953	1960
170	1967	1974	1981	1988	1995	2002	2009	2016	2023	2030
180	2036	2043	2050	2057	2063	2069	2076	2082	2088	2095
190	2101	2106	2113	2118	2125	2139	2137	2143	2149	2155

TABLE X (cont'd)

Log Log (K + .8) x 10,000

Compiled from A.S.T.M. equations
and 7 place logarithm tables

Saybolt Visc.	0 50	05 55	10 60	15 65	20 70	25 75	30 80	35 85	40 90	45 95
200	2161	2189	2217	2244	2270	2295	2320	2344	2367	2389
250	2412	2433	2454	2474	2494	2514	2533	2552	2570	2588
300	2605	2622	2639	2655	2671	2687	2703	2718	2733	2748
350	2762	2776	2790	2804	2817	2830	2843	2856	2869	2881
400	2893	2905	2917	2929	2940	2951	2963	2974	2984	2996
450	3006	3016	3026	3038	3046	3056	3066	3076	3085	3094

	0	10	20	30	40	50	60	70	80	90
500	3104	3122	3140	3157	3174	3191	3207	3223	3238	3253
600	3268	3285	3297	3311	3325	3339	3352	3365	3378	3391
700	3403	3415	3427	3439	3450	3462	3473	3485	3495	3506
800	3516	3527	3537	3547	3557	3567	3576	3586	3595	3605
900	3614	3623	3632	3641	3649	3658	3666	3675	3683	3691

TABLE X (cont'd)

Log Log (V + .8) x 10,000

Compiled from A.S.T.M. equations
and 7 place logarithm tables

Saybolt Visc.	0 500	50 550	100 600	150 650	200 700	250 750	300 800	350 850	400 900	450 950
1000	3699	3738	3775	3810	3843	3875	3905	3934	3961	3988
1500	4013	4037	4061	4084	4106	4127	4147	4167	4186	4205
2000	4223	4240	4258	4274	4290	4306	4321	4336	4351	4365
2500	4379	4393	4406	4419	4432	4444	4456	4468	4480	4491
3000	4503	4514	4524	4535	4546	4556	4566	4576	4585	4595
3500	4604	4614	4623	4632	4640	4649	4658	4667	4675	4683
4000	4691	4699	4706	4714	4722	4730	4737	4744	4751	4758
4500	4765	4772	4779	4786	4793	4800	4806	4813	4819	4825
5000	4831	4837	4843	4849	4855	4861	4867	4873	4879	4885
5500	4890	4896	4901	4907	4912	4917	4922	4928	4933	4938
6000	4943	4948	4953	4958	4962	4967	4972	4977	4982	4987
6500	4991	4996	5000	5005	5009	5014	5018	5022	5026	5031
7000	5035									
7500	5075									
8000	5113									
8500	5148									
9000	5181									
9500	5212									
10,000	5241									

TABLE XI

Data is taken from Moore's "Molecular Weight and Absolute Viscosity of Lubricating Oils" and the cube root of the absolute viscosity is calculated using Moore's values for the mean molecular weights and mean molecular weights determined using stearic acid as a solvent. Kendall and Monroe cube root equation for binary mixtures was used.

Blend No.	Mole % Ccomp.	Saybolt Seconds 210° F	Density 210° F	Absolute Viscosity	$(n)^{1/3}$ Determined	Calc $(n)^{1/3}$ $C_2H_4Br_2$	Calc $(n)^{1/3}$ Stearic Acid
1.	25A 75D	122	.870	.2239	.6072	.5891	.5910
2.	50A 50D	87	.869	.1514	.5330	.5162	.5186
3.	75A 25D	62	.869	.0944	.4553	.4433	.4451
45.	30.0I 70.0J	117	.846	.2080	.5925	.5852	.5930
46.	61.5I 38.5J	79	.842	.1296	.5060	.4913	.5017
47.	82.5I 17.5J	60	.835	.0861	.4416	.4340	.4352
48.	93.3I 6.7J	49	.829	.0588	.3888	.3964	.3993

Plate I

Relation of K for $C_2H_4Br_2$ To Freezing Point Lowering

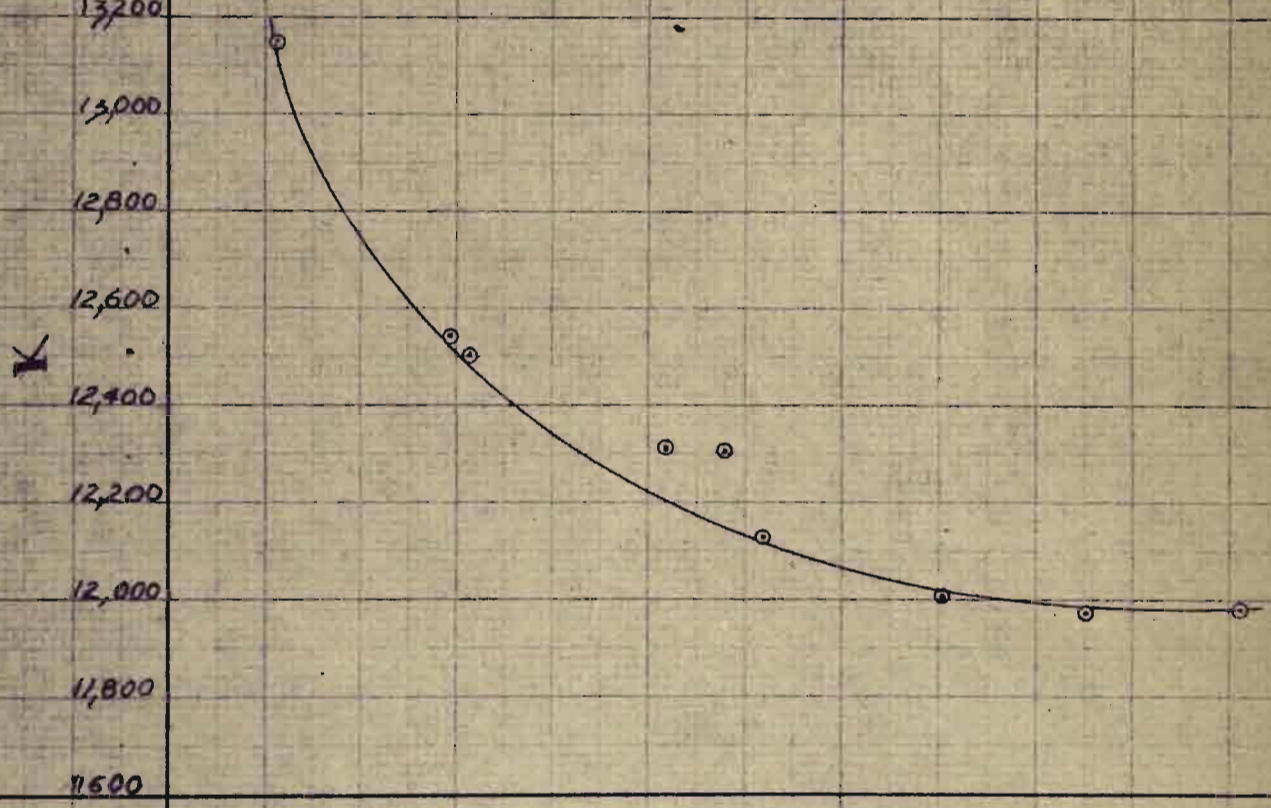


Plate II

Blends of Shell 200 Golden Neutral and Parowax (A and W)

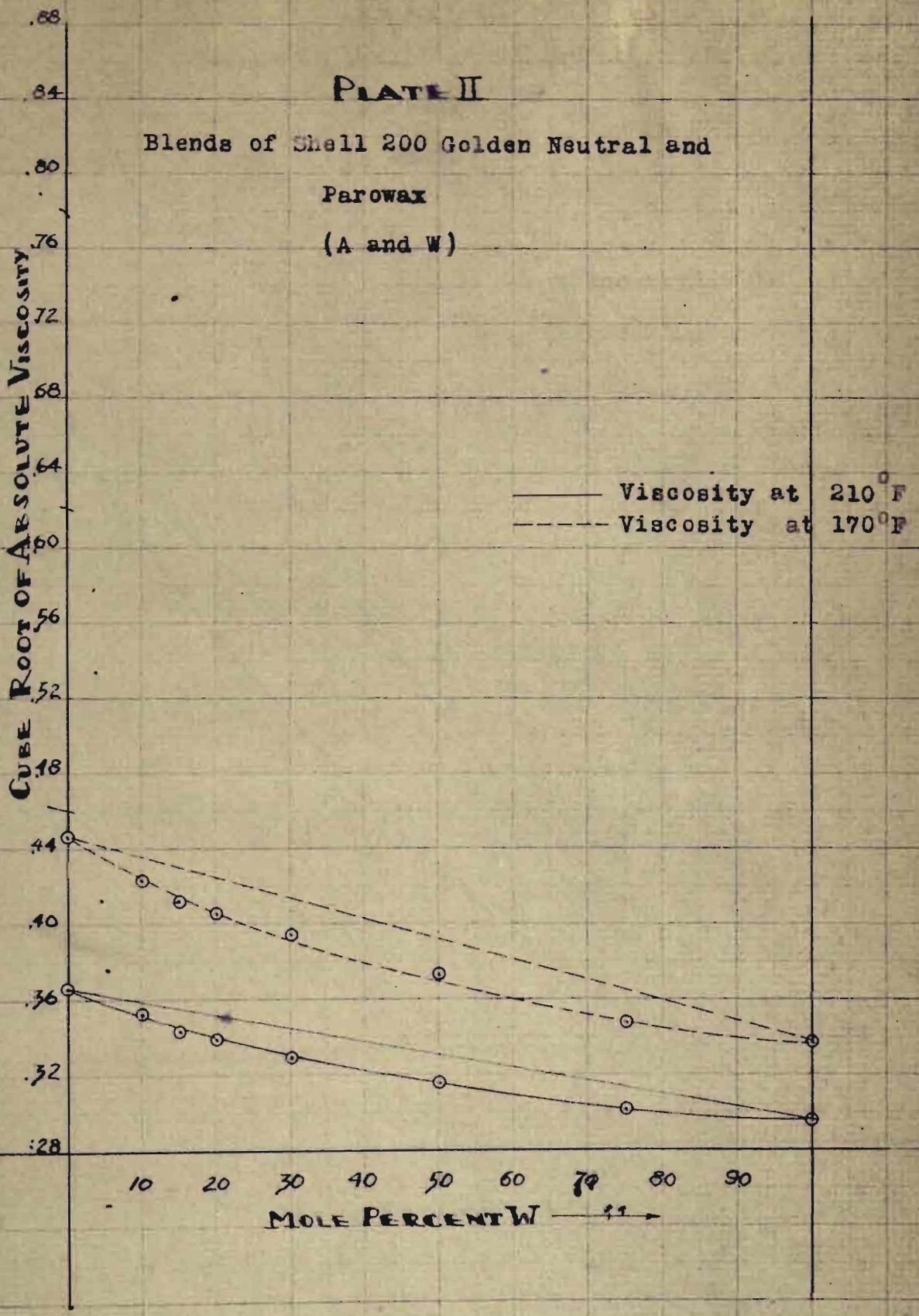


PLATE III

Blends of Shell "H" Bright Stock and Parowax

(D and W)

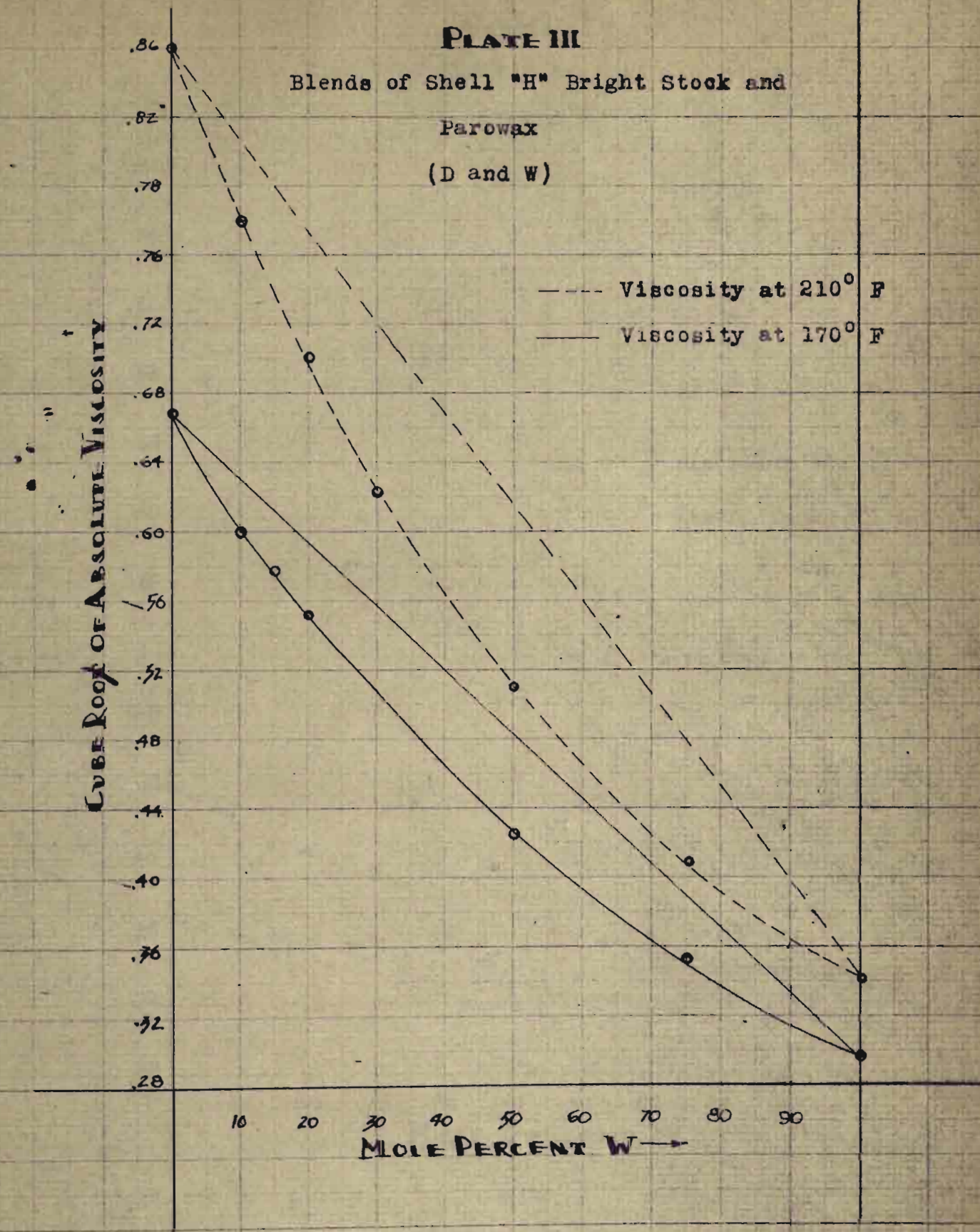


Plate IV

Blends of Kendall Neutral and Parowax

(I and W)

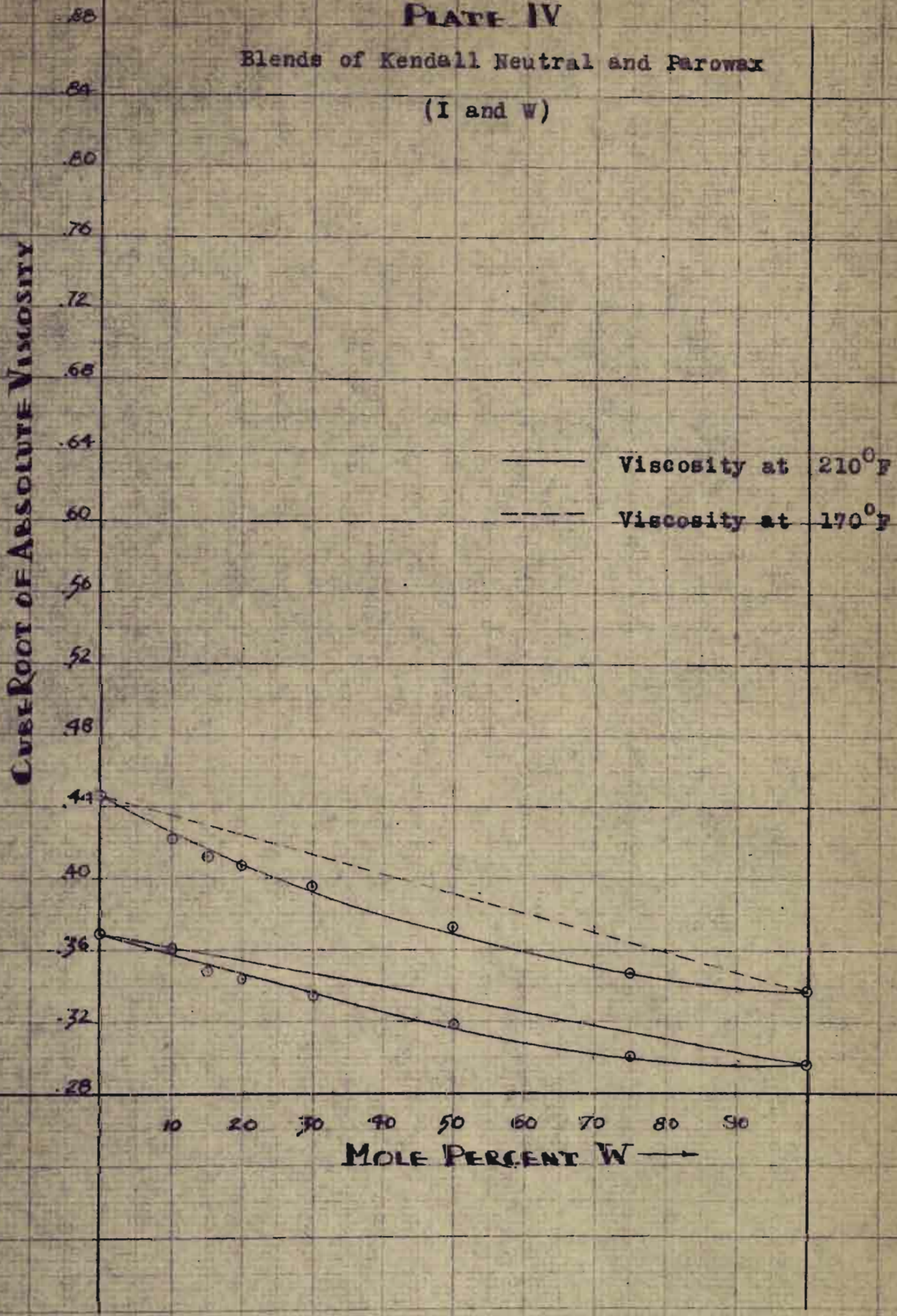


Plate V

Blends of Kendall Bright Stock and Parowax (J and W)

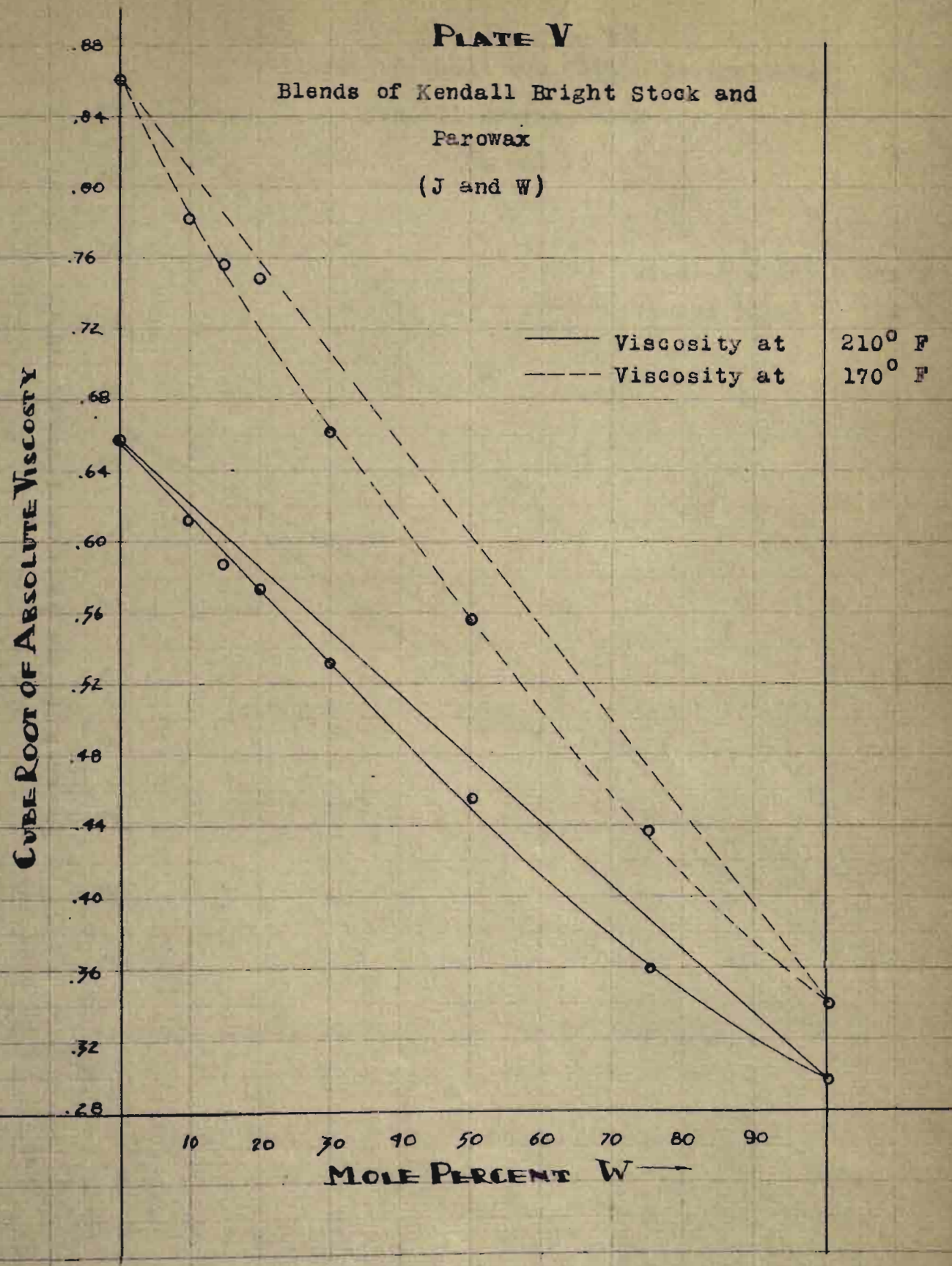


Plate VI

Blends of Shell 200 Golden Neutral and ~~Kendall Bright Stock~~ (A and J)

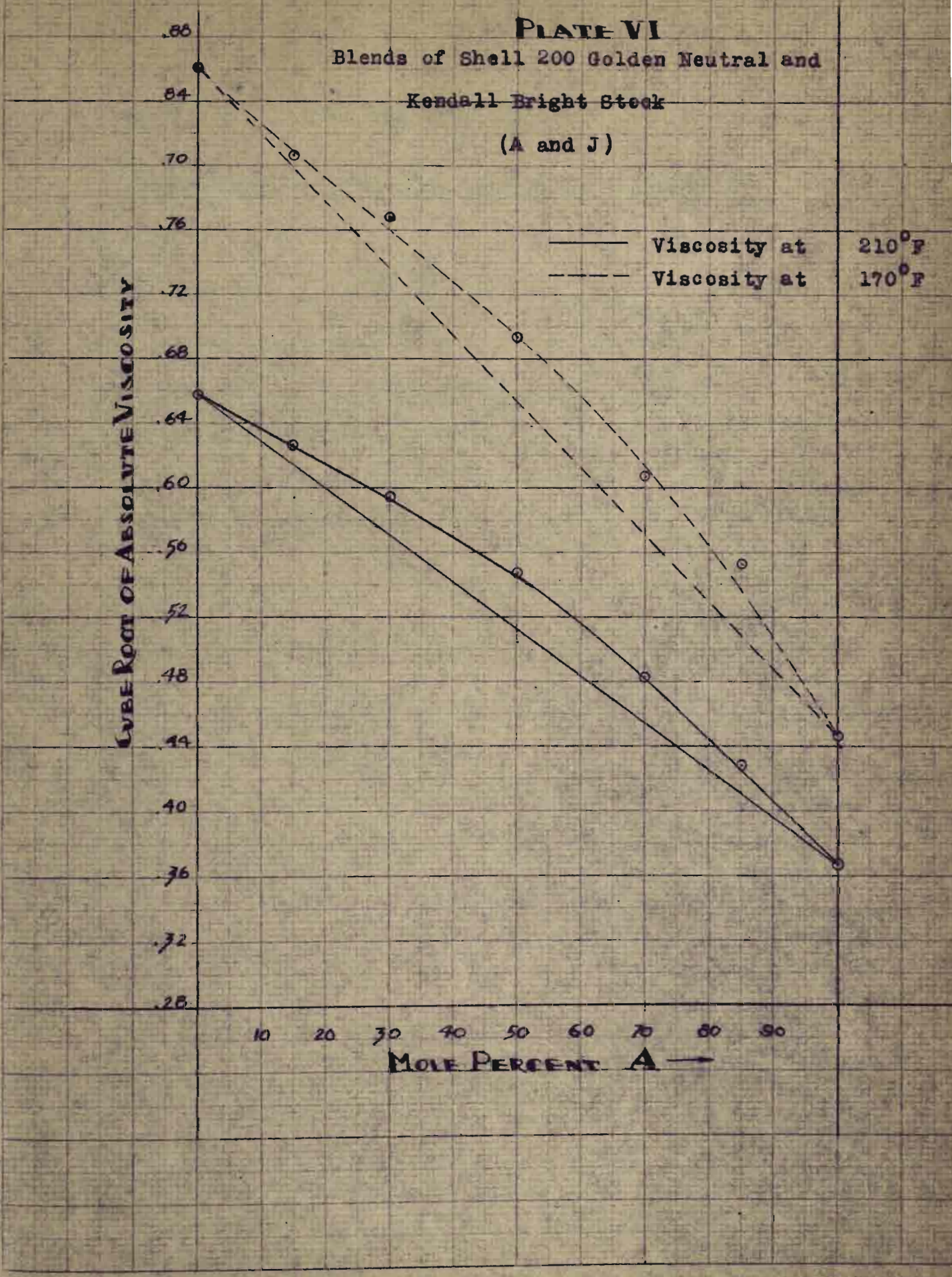
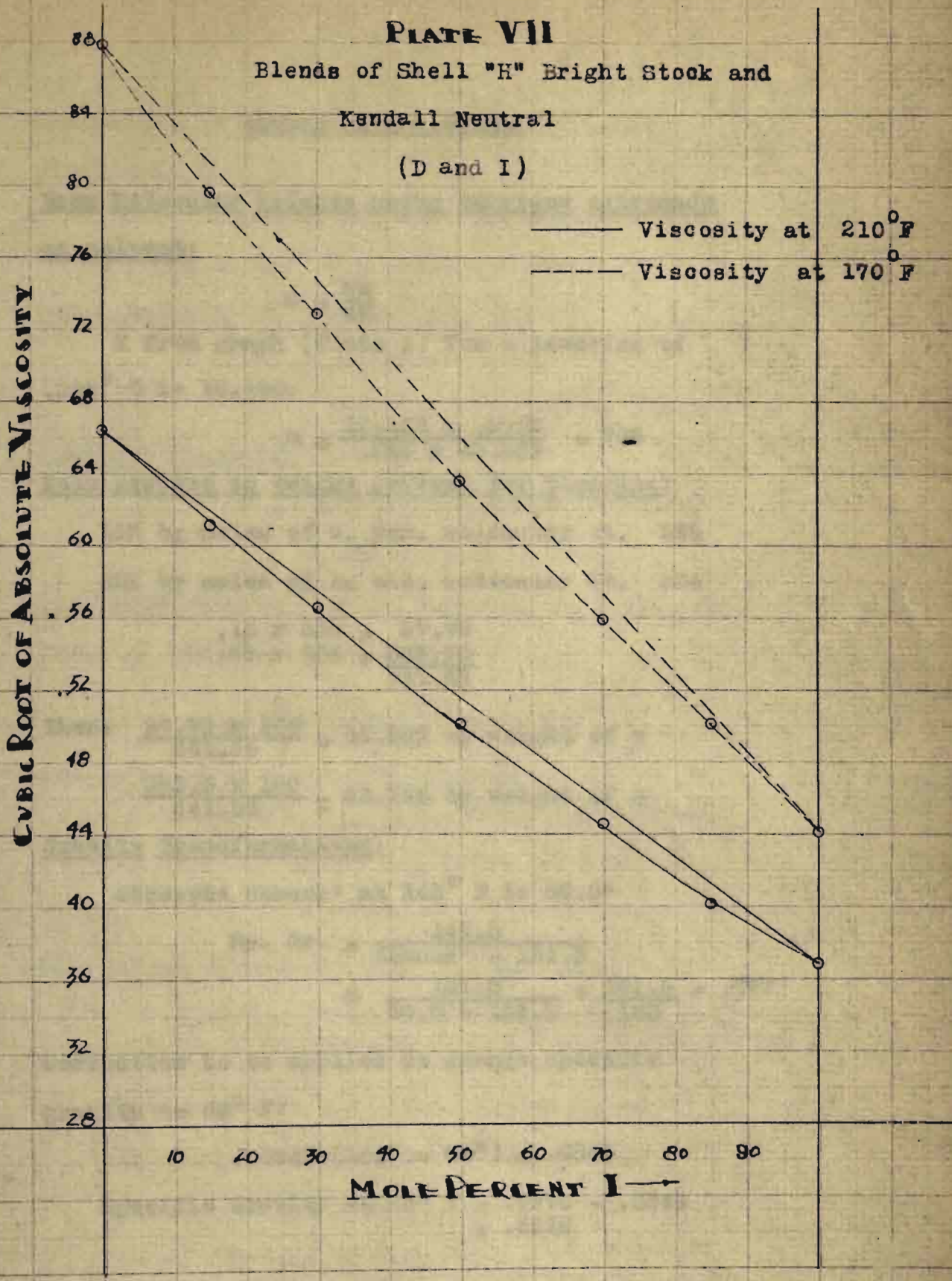


Plate VII

Blends of Shell "H" Bright Stock and Kendall Neutral

(D and I)



SAMPLE CALCULATIONS

Mean Molecular Weights using Ethylene dibromide as solvent:

$$m = \frac{Kw}{dW}$$

K from graph (Plate I) for a lowering of .225° C is 12,450.

$$m = \frac{12,450 \times .5705}{.225 \times 45.369} = 706$$

Mole percent to weight percent for blending:

15% by moles of W, wax, molecular Wt. 385

85% by moles of A, oil, molecular Wt. 334

$$\begin{aligned} .15 \times 385 &= 57.75 \\ .85 \times 383 &= \underline{383.90} \\ & \quad 341.55 \end{aligned}$$

Then, $\frac{57.75 \times 100}{341.55} = 16.88\%$ by weight of W

$\frac{383.9 \times 100}{341.55} = 83.12\%$ by weight of A

Gravity Transformations:

Observed Beaume' at 143° F is 50.5'

$$\text{Sp. Gr.} = \frac{141.5}{\text{Beaume}' - 131.5}$$

$$= \frac{141.5}{50.5 - 131.5} = \frac{141.5}{182} = .777$$

Correction to be applied to change specific gravity to 60° F:

$$.00042\ (143^\circ - 60^\circ) = .0349$$

Specific Gravity at 60° F = .7770 - .0349

= .8119

Correction to be applied to change Specific Gravity to 210° F:

$$.00042\ (60 - 210) = -.0630$$

Sp. Gr. at 210° F = .8119 - .0630 = .7489

Calculation of Kinematic Viscosity:

$$n/d = .00226\ t - \frac{1.95}{t}$$

$$= .00226 \times 38 - \frac{1.95}{38} = .03456$$

Absolute Viscosity:

n = Kinematic Viscosity x density

= .03456 x .7489 = .0259

Valuation of cube root of viscosity of blend, by means of Kendall's equation:

$$(n)^{1/3} = X_1(n_1)^{1/3} + X_2(n_2)^{1/3}$$

50% by moles of W and 50% by moles of A

$$(n)^{1/3} = .50(.0259)^{1/3} + .50(.0492)^{1/3}$$

$$= .50 \times .2956 + .50 \times .3665$$

$$= .3310$$

Calculation of blends using the equation:

$$\text{Log Log } (K + .8) = X \text{ Log Log}(K_1 + .8) + (1 - X) \text{ Log Log } (K_2 + .8)$$

Viscosity of A in Saybolt Seconds = 60

Viscosity of B in Saybolt Seconds = 80

Volume fraction of A = .1

Volume Fraction of B = .9

From Table X find value of LogLog (K_1+.8) x 10000 is for A is + 0194, and for B is + 0849

Then:

$$\text{LogLog } (K + .8) \times 10{,}000 = .1 \times 0194 + .9 \times 0849$$

$$= 0783$$

Then finding viscosity corresponding to 0783, interpolating between 0774 and 0800, to be 77.3 Saybolt seconds.

DISCUSSION OF RESULTS

Stearic acid was found to be a satisfactory solvent for cryoscopic determination of mean molecular weights of lubricating oils and paraffin waxes. It is only slightly hydroscopic and no great caution is required to keep it dry.

Para dichloride of benzene was found to be unsatisfactory for cryoscopic work as it would condense in the upper part of the freezing point tube and consistently give lower thermometer readings for its freezing point. The time required for the temperature to reach a maximum was about twice as long as that required for stearic acid.

An examination of Plates II to VII will show that the cube root of the absolute viscosity of blended lubricating oils is not a simple linear function of the relative number of molecules of its components. Blends of lubricating oils and paraffin wax show a greater deviation than blends of lubricating oils from the calculated values as determined by the Kendall and Monroe equation. The less classical equation of Fitz Simons seems to approximate the experimental value more closely.

$\underline{K}$ for stearic acid was found to be 4410.

SUMMARY

The mean molecular weight of lubricating oils determined in stearic acid as a solvent, show a lower molecular weight than when they are determined in ethylene dibromide, benzene, or nitrobenzene. The mean molecular weights of paraffin waxes can be determined in stearic acid as a solvent. The probable carbon atom content of these waxes ranges from twenty-three to twenty-nine if they are considered as saturated open chain compounds.

The cube root of the absolute viscosity of a blend when plotted against the mole percent as abscissa tends to arch. This arching would indicate a tendency for the molecules of lubricating oils to associate. On the other hand when waxes are blended with lubricating oils in like manner, the curves tend to sag very markedly. This would tend to indicate that the paraffin wax tends to cause the lubricating oil molecules to dissociate, that is the aggregates of molecules break down into simpler molecules.

In most cases the Fitz Simons equation apparently comes nearer enabling the blender to estimate the viscosity of a blended oil.

PARTS OF APPARATUS

A. Fused calcium chloride drying tower.

B. Sulphuric acid bubbling tower.

C. Cotton dust filter.

D. Beckmann freezing point tube ensemble.

E. Rehostat control for electric motor.

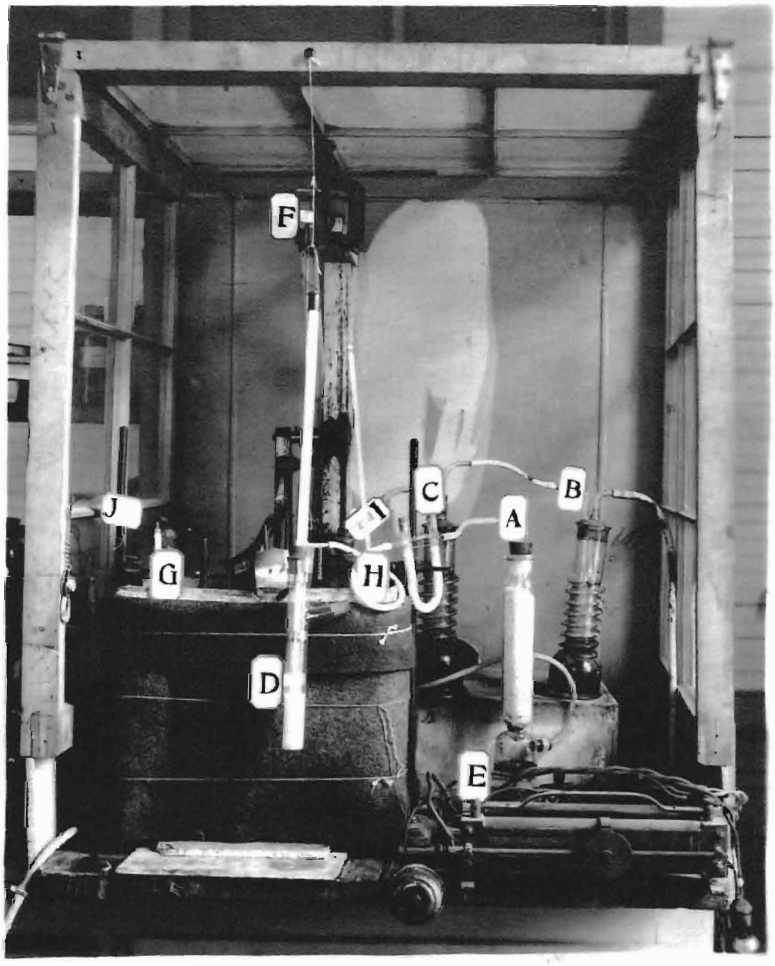
F. Power pulley of mechanical stirrer.

G. Heating bath.

H. Cooling bath.

I. Electric heater for temperature control of cooling bath.

J. Electric heater for temperature control of heating bath.



Beckmann Freezing Point Apparatus Equipped

For High Temperature Freezing Point Determination.

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